CBD SBIR Phase 2 Final Report:
Improved Chemical Protective Gloves using Elastomeric Nanocomposites

Harris A. Goldberg and Carrie A. Feeney

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The Innovative Materials Company

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InMat LLC
Hillsborough, NJ

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1. Abstract

Nanocomposite Coatings of neoprene and nitrile Rubber based on InMat's environmentally friendly, water based, Nanolok coating technology have been developed. In this report, we discuss the optimization and scale up of these coating formulations that are targeted for use in multilayer chemical protective gloves. Such gloves will provide the protection of butyl based gloves while having significantly improved resistance to petroleum oils and gasoline while also being less flammable. There is also the potential for making these gloves significantly thinner than the currently used butyl rubber gloves.

This report also discusses the details of permeation through multilayer structures, and shows how to model both the steady state permeation rate and the kinetics. It is the short time kinetics after initial exposure to a chemical warfare agent (CWA) that is critical to determining the protection. The modeling work described here is used to demonstrate that the use of nanocomposite barrier layers in a multilayer structure provide some surprisingly important dependence on the details of how the barrier is deployed in the structure. This work has led to a patent application, and has been verified using

detailed studies of the kinetics of helium permeation. Initial work on solvents and CWA simulants is also presented to further demonstrate the potential of this multilayer approach.

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4. Preface: Description of Project & Objectives

The overall objective of this program is to finalize the multilayer glove design and coating formulation that provides 24 hours of protection against chemical warfare agents while having better flame and POL resistance than butyl rubber gloves.

In particular, the work here is targeted at developing stable, practical, nanocomposite barrier coating formulations that can be combined with neoprene and/or nitrile rubber to produce gloves which provide the protection from chemical warfare agents of butyl gloves but with improved resistance to

petroleum oils and reduced flammability offered by nitrile and neoprene. Neoprene offers an excellent combination of petroleum oil resistance and flame resistance. Its barrier to chemical warfare agents, however, is not adequate for protective glove applications. Nitrile rubber offers excellent petroleum oil resistance, but it is also not adequate for protection against some chemical warfare agents. The focus of this project is to develop nanocomposite barrier coatings that can be used in multilayer designs with neoprene and nitrile rubber to provide the barrier to chemical warfare agents equivalent to the butyl rubber gloves currently in use.

5. Acknowledgements

6. Methods, Assumptions, Procedures & Materials

6.1. Chemical Warfare Agent (CWA) Testing

All chemical warfare testing was done at Geomet Technologies Inc., Laboratory Division using MIL-STD-282: Military Standard Filter Units, Protective Clothing, Gas-Mask Components and Related Products: Performance-Test Methods, Office of the Assistant Secretary of Defense, Washington, 25, D.C., Supply and Logistics, 28 May 1956, and Notice 4, 12 January 1995:

Method 208.1: GB Resistance of Impermeable Materials (Static Diffusion Method). Quantitative – Analyze for ug/cm2 of agent penetrated.

Method 209.1: HD Resistance of Impermeable Materials (Static Diffusion Method). Quantitative – Analyze for ug/cm2 of agent penetrated.

6.2. Oxygen Transmission Rate Testing

Films and coated substrates are tested for oxygen transmission rate using a Mocon OXTRAN 2/20 or 2/60 module at 23C and 0% RH. The samples are loaded onto the modules and conditioned for 2 hours prior to testing for oxygen. Once equilibrium is reached, an OTR (oxygen transmission rate) is reported in units of cc/m2 day atm.

6.3. Thickness Measurements

The thickness of the coating on a substrate is measured after the OTR is reported. Each sample is removed from the Mocon module and a circle of specified size cut from the sample. The cut circle is weighed. The weight of the coating is obtained from subtracting the weight of the uncoated circle and the thickness calculated from the size of the circle and weight of the coating. The thickness of the film is reported in millimeters and used to calculate the permeability of the film.

6.4. Permeability Calculations

Permeability is calculated using the thickness of the film and the OTR of the sample in the following equation:
Coating Permeability = (coating thickness)/[(1/OTR)-(substrate thickness/substrate permeability)].

The benefit of obtaining the permeability of the coating versus the OTR of the sample is that permeability reports the OTR at a specified thickness. Therefore, different coatings can be compared directly. This is important when determining the performance of a coating on varying substrates and at different thickness'.

6.5. Helium Permeation Rate Testing

Helium permeation measurements are made using an internally developed apparatus. Prior to a measurement, a sample is thoroughly degassed from both sides with a vacuum pump. The system determines gas transmission through a sample by exposing one side of the sample to a step change in gas pressure and measuring the rise in pressure in a known volume on the other side of the sample with a capacitance manometer. The pressure vs. time data is acquired and a numerical derivative calculated which is used to determine both the steady-state permeability and the initial kinetics of the gas transmission.

6.6. Strain Measurements

This test determines the percent strain on a sample when first visual damage occurs. This is an InMat designed and built test. A 2"x2" coated substrate is mounted on a specifically designed pressure clamp in a humidity controlled chamber. The sample is strained biaxially using controlled amounts of compressed air in 1 pound increments. The sample is viewed during this test using a Leitz zoom stereomicroscope at 16x magnification and videotaped. The % strain when damage first occurs is calculated by the change in the distance of the fiducial marks on the sample.

6.7. Materials

The following substrates were used for each test or measurement:

OTR measurements: Biaxially oriented polypropylene, Hoechst, 0.02 mm
Strain measurements: Ethylene-propylene-diene copolymer (EPDM), McMaster-Carr, 0.8 mm
CWA testing: Biaxially oriented polypropylene, Hoechst, 0.02 mm
                      Ansell Edmont unsupported Neoprene glove, Lab Safety, 14 mil
                      Unfilled natural rubber, McMaster-Carr, 0.7 mm

Helium measurements: Unfilled natural rubber, McMaster-Carr, 0.7 mm

7. Work Performed & Results

7.1. InMat Technology Platform

InMat has led the development of aqueous nanocomposite coatings that provide large reductions in the permeability of the matrix polymer by the incorporation of nano-dispersed clay. Such coatings have been commercialized in Wilson's Double Core tennis balls, the official ball of the Davis Cup, and are being tested in a wide variety of other applications. For more information refer to the InMat web page. [1]

InMat is currently commercializing barrier coatings based on glassy polymers for use in the food packaging industry where the oxygen permeability of the matrix polymer has been reduced by a factor of 1000. For applications in protection against chemical warfare agents, elastomeric coatings are desired. The objective is to develop gloves and other protective equipment with long breakthrough times that do not have the deficiencies of currently used butyl rubber such as sensitivity to petroleum oils and flammability. In addition, it is expected that this technology will lead to gloves that are thinner and provide improved dexterity.

As part of this effort, InMat has developed elastomeric nanocomposite coatings based on several different elastomers as shown in Table 1 below.

Table 1. Large Oxygen Permeability Reductions Demonstrated with Several Elastomers

Latex Type	% Filled	Permeability[1]	Times Reduction	% Strain	Key Secondary Properties
Butyl	50	0.3	300	10	Low Temperature Flexibility
Butyl	30	1.2	75	15	
Butyl	20	2.5	36	20	
Butyl	0	90			
Chloroprene	30	1.5	83	12	Ozone, UV, oil & solvent resistance
Chloroprene	0	125			
Nitrile	30	2.3	57	14	Solvent, oil & fuel resistance
Nitrile	0	130			
EPDM	20	17	11	15	Ozone, UV, sunlight, steam, brake fluid, & weak acid resistance
EPDM	0	185			

Note 1: Permeability is oxygen permeability in units cc mm/m^2 day atm @ 23C, 0% RH.

Large reductions in oxygen permeability can be achieved while maintaining adequate flexibility for use in chemical protective equipment. All InMat coatings are water based and contain no hazardous materials. The % strain numbers in Table 1 refer to the strain at which any damage occurs during a biaxial stretch at room temperature and 0% humidity as described in reference [2]. Larger strains will begin to degrade the barrier properties, but not in a catastrophic manner.

Since the reduction in oxygen permeability is due to the tortuous path created by the dispersed clay, it is expected that similar reductions in permeability will be achieved for other permeants. Permeants with large specific absorption on the clay surface, or that significantly swells the polymer matrix will have more complicated behavior.

7.2. Formulation
The neoprene and nitrile nanocomposite data cited below were used as examples for a U.S. patent application and an international patent application to add to the technology previous covered by InMat's U.S. patents 6,087,016 and 6,232,389.

Summary of Accomplishments

- There has been significant improvement in both shear and overall formulation stability of the neoprene based nanocomposites.
- These improved neoprene nanocomposite formulations were successfully scaled to 2 gallons and evaluated by Best Manufacturing.
- Nitrile based nanocomposites were also developed. Coatings made from these formulations have much lower permeability and higher strain to first damage than the neoprene nanocomposites.
- The stability and adhesion to rubber substrates of the nitrile nanocomposites were significantly improved. The improved formulations have been produced in 2 gallons batches.

7.2.1. Neoprene based Nanocomposites

The initial formulation work in phase 2 was done to improve the neoprene based nanocomposites developed in phase 1 and phase 1 option. Many variables such as additives, filler treatment, pH, adhesion promoters and cure packages were modified to improve formulation stability, shelf life, shear stability and strain to first failure. Additionally, work was done to scale up the formulation and periodically sample Best Manufacturing to produce gloves and provide overall feedback during glove dipping. Table 2 below summarizes the best case formulations at different stages during the first year of phase 2. Finally, the progress from phase 1, phase 1 option and phase 2 year 1 are compared. Table 3 below summarizes the performance of the scaled up formulations (2 gallons).

Table 2. Formulation Modifications to Neoprene Nanocomposites – Nanolok NP

Formulation	Details	Permeability[a]	Strain[b]	Stability[c]
Neoprene 750	Phase 1 results	1.4	n/a	n/a
Neoprene 400	Phase 1 option results	0.6[d]	-/8	√
Neo 571/671 blends	Best case additives modification	3.3	-/17	√
Neo 571/671 blends	Best case alternate treatment	2.8	10/10	√
Neoprene 571	Best case combination with additives, treatment & pH	2.0	2/13	√
Neoprene 671A	Change in Neoprene grade with additives modification	2.2	-/11	+
Neoprene 571A	Best combination of grade, additives, pH, treatment	1.7	8/15	++
Neoprene 571A 38761-76-2d	Combination above with Humectants & Curatives Phase 2 Year 1 Result	1.7	15/15	++

Notes:
a) Permeability is oxygen permeability reported in cc mm/m2 day atm @ 23C, 0% RH.
b) Strain is reported as % strain at first visual damage. The first number is damaged with the second number as actual cracking.
c) Stability is determined by stirring overnight. A negative mark indicates instability, a check mark indicates moderate stability and a plus mark indicates good stability beyond 24 hours of stirring.
d) This permeability may be unusually low due to the effect of the high chlorine content of Neoprene 400 effecting the readout of the Mocon oxygen analyzer.

Table 3. Scale-up Results of Neoprene Nanocomposites

Formulation	Details	Permeability[a]	Strain[b]	Stability[c]
38761-19-2	Neoprene 571 October 2003	2.1	5/15	√
38761-29-1	Neoprene 571 January 2004	2.0	-/8	-
38761-52-1	Neoprene 571 March 2004	1.4	12/16	-/√
38761-63-2	Neoprene 571 April 2004 Scaled up Phase 2 Year 1 Result	1.7	8/15	++

Notes:
  a) Permeability is oxygen permeability reported in cc mm/m^2 day atm @ 23C, 0% RH.
  b) Strain is reported as % strain at first visual damage. The first number is damaged with the second number as actual cracking.
  c) Stability is determined by stirring overnight. A negative mark indicates instability, a check mark indicates moderate stability and a plus mark indicates good stability beyond 24 hours of stirring.

There had been significant improvement in both shear and overall stability during year 1 of phase 2. In addition, a better combination of low permeability and high strain to first failure was achieved. Although initial feedback from Best was positive, it was later determined that improvements in the neoprene stability and shelf life was required.

We retested neoprene formulations for aging effects on permeability, viscosity, pH and strain. The results are listed in Table 4. From the table, the one variable that is inconsistent is viscosity. This variable will be targeted for future work since viscosity is critical for glove dipping. The strain evaluation is still ongoing. The permeability in all cases was improved. This is consistent with data from the Air D-Fense 2000 butyl based formulations. The pH is relatively stable with the exception of one formulation.

Table 4. Aging Evaluation of Neoprene nanocomposite

Formulation	Age	Permeability[1]		Strain[2]		Viscosity[3]		pH	
		Initial	Current	Initial	Current	Initial	Current	Initial	Current
38761-79-2a 2% humectant A added last	5 months	1.9	1.8	11	n/c	700	4500	10.5	10.7
38761-79-2b 2% humectant A added to matrix	5 months	2.1	1.7	10	n/c	900	750	10.5	10.6
38761-86-1 2% humectant B added last	4 months	1.4	1.3	6	n/c	1010	5500	10.2	10.4
38761-79-2a2 repeat of 1st entry	3 months	2.7	1.9	9	n/c	1200	1400	10.3	11.1

Notes:
  1. Permeability is oxygen permeability in units of cc mm/m^2 day atm at 23C, 0% RH.
  2. Strain is biaxial strain reported in % at 12% RH. The n/c designation indicates test not complete.
  3. Viscosity is reported in units cP at 25C.

Based on feedback during sampling with customers, there may be an issue with the stability of these formulations during shipping. This is an area that will require additional work before full commercialization.

7.2.2. Nitrile Nanocomposites

Since Best Manufacturing was using some nitrile glove substrate for the proposed protective glove, we started to evaluate nitrile latex as the nanocomposite matrix. Dow Reichhold supplied us with a variety of nitrile latices that we evaluated based on the previously developed neoprene nanocomposite technology. This class of latex is easier to work with because it doesn't skim as quickly and the pH is neutral (neoprene latex has a pH of 10-12). Table 5 below shows the progress made using nitrile based latices. Since the permeability and strain were much improved using the nitrile latex (as compared to the neoprene latex in Tables 2,3 & 4), the initial try of nitrile 68085 was also scaled to 2 gallons and sampled to Best Manufacturing. This formulation did not have adequate stability when received at Best Manufacturing. The subsequent formulation changes have shown increased stability and adhesion.

Table 5. Formulation of Nitrile Nanocomposites – Nanolok NT

Formulation	Details	Permeability[a]	Strain[b]	Stability[c]
Nitrile 68073 (General)	Best case	2.3	14/14	√
Nitrile 68829	Initial try	2.4	-/11	√
Nitrile 97767	Initial try	6.8	-/10	√
Nitrile 68766	Initial try	5.0	-/7	√
Nitrile 68085	Initial try	1.0	-/25	- poor adhesion
Nitrile 68085	**Modified additives & pH process**	1.1	-/22	+
Nitrile 68085	**Initial with curatives**	1.4	-/25	√ improved adhesion

Notes:
   a) Permeability is oxygen permeability reported in cc mm/m^2 day atm @ 23C, 0% RH.
   b) Strain is reported as % strain at first visual damage. The first number is damaged with the second number as actual cracking.
   c) Stability is determined by stirring overnight. A negative mark indicates instability, a check mark indicates moderate stability and a plus mark indicates good stability beyond 24 hours of stirring.

Based on feedback from Best, it was determined that the above formulations needed additional improvements in adhesion. It was also determined that optimization of the cure package was the most likely way to improve adhesion. Work was therefore started to screen a larger range of cure packages. We ordered samples of everything and made a master batch of curatives. The initial results are listed below in Table 6. The modified curatives show a modest improvement in permeability. We continued to modify the curatives system and the additional results are listed in Table 6 as well.

Table 6. Formulation of Nitrile Nanocomposites – Modified Cure Packages

Formulation	Curatives phr[1]	Permeability[2]
	Initial – no curatives	2.6
	Initial package – 1 phr	1.6
38763-04-2a	New package – 1 phr	1.9
38763-04-2b	New package – 2.5 phr	1.8
38763-04-2c	New package – 5 phr	1.5
New Formulation Work		
38763-07-1	New package – 12 phr	1.4
38763-08-1	New package – 20 phr	1.4
38763-08-2	Stepwise addn – 12 phr	1.8

Notes:
1. phr is parts per hundred rubber of the cure package.
2. Permeability is oxygen permeability in units cc mm/m^2 day atm @ 23C, 0% RH.

The adhesion test that was used to evaluate the cure packages was the cross hatch adhesion test. The cross hatch is put into the coating and then a specific tape is used on the cross hatch. The amount of material left is determined by the approximate percentage of the area. This is not a quantifiable amount. It is more of a "better/worse" test. In the previous results, the new cure package showed a modest improvement on the cured EPDM substrates. We increased the amount of the cure package and again only saw a modest improvement in adhesion. The real improvement in adhesion was to change the curatives to a stepwise process as opposed to formulating a master batch. As demonstrated in the last entry of Table 6, the permeability did increase somewhat but the adhesion was much improved. We will continue to monitor shelf life of this material. This material has been scaled up to 1 gallon batches and has been shown to have adequate stability and shelf life.

After this work was completed, our nitrile supplier (Dow Reichhold) informed us that they could no longer supply the nitrile we had been using. We therefore searched for an alternative supplier. After screening a large number of potential nitrile candidates, we were successful using Chemigum 550 from Eliokem. This formulation has been shown to provide similar performance to that obtained with Dow Reichhold's material, and has been scaled up to 2 gallons and sent to a customer for evaluation.

Table 7. Formulation of Nitrile Nanocomposites – Eliokem Chemigum 550 Alternative

Formulation	Details	Permeability[a]	Viscosity[b]	pH/Stability
38763-21-1	Initial	1.2	45 cP @ 45 rpm	8.6/√
38763-22-1a	Modify viscosity	1.3	1552 cP @ 45 rpm	6.7/√
38763-22-1a	Scale up previous	2.2	agglomerated	--
38763-22-1b	Modify pH	1.1	77 cP @ 30 rpm	9/√
38763-23-1a	Scale up previous	1.3	349 cP @ 1 rpm	9.2/√
38763-23-1b	Modify 22-1a pH & scale up	1.3	42 cP @ 22 rpm	7.6/+
38763-23-1c	Modify 22-1a pH & scale up	0.8	42 cP @ 12 rpm	7.7/-

Notes:
a) Permeability is oxygen permeability reported in cc mm/m^2 day atm @ 23C, 0% RH.
b) Viscosity is measured with a Brookfield DVII+ Viscometer using the small sample adaptor with spindle #18 at 25C.

c) Stability is determined by stirring overnight. A negative mark indicates instability, a check mark indicates moderate stability and a plus mark indicates good stability beyond 24 hours of stirring.

7.3. Glove Process

Summary of Accomplishments

- A glove dipping process was developed for the nanocomposite materials. This was significant progress because the standard process of coagulant dipping could not be used with InMat materials.
- Simulant testing was put in place using ASTM F739 at our glove partner location.
- A variety of polymers were evaluated as the glove matrix with priority given to neoprene and nitrile latices.
- Identified heat sensitized material to use with Air D-Fense 2000R to obtain thicker coatings.
- A variety of glove prototypes were made and tested at Best and at InMat.
- Testing of InMat formulations has begun at other protective glove manufacturers.

7.3.1. Dipping Process

Best Manufacturing established a dipping procedure to use as a guide in dipping polymer films. A critical aspect of this process was to ensure that each dip layer is completely dry before the next layer is applied. If any of the layers are not dry, delamination between layers would occur.

Using this dipping process, Best evaluated many different polymers as the base material for the glove. They evaluated different grades of neoprene latex, nitrile latex, SBR latex and combinations of each. They also evaluated wetting and flow issues in conjunction with InMat's butyl, neoprene and nitrile based nanocomposites. One of the initial problems they encountered was with the butyl based nanocomposite, Air D-Fense 2000R (AD2000R). There was no adhesion with AD2000 and the nitrile or Neoprene layers. This obstacle was overcome by using the neoprene based nanocomposite (Nanolok NP) or the nitrile based nanocomposite (Nanolok NT).

7.3.2. Glove Prototypes & Testing

Best Manufacturing focused initially on assessing many different glove designs using the butyl based nanocomposite, Air D-Fense 2000R. Once InMat was able to provide Best with the neoprene based nanocomposite (Nanolok NP), they began designing gloves with that material. It was much easier to work with to provide uniform coatings with adequate adhesion to the rubber substrates. Table 8 summarizes the initial gloves developed using both the butyl based nanocomposite, Air D-Fense 2000R, and the neoprene based nanocomposite, Nanolok NP.

Table 8. Initial Glove Prototypes by Best Manufacturing

Glove	Inner layer	Barrier Layer[a]	Outer Layer	Comments
September 2003 Batch of Gloves				
1	Nitrile 68073	AD x 3	Neoprene 750	Poor adhesion. Only tested for perchloroethylene
2	Neoprene	AD x 3	SBR	Surface tension problem w/ AD

3	Nitrile 68073	AD x 3	SBR	Surface tension problem w/ AD
4	SBR	AD x 3	SBR	Surface tension problem w/ AD
5	Nitrile 68073	AD x 1	Neoprene & MAA Copolymer	No resistance to chemicals
6	Butadiene Goodrite SB1177	AD x 1		Delamination due to incomplete drying
center	November 2003 Batch of Gloves			
1	Nitrile 68085	AD x 1	Polyurethane WitcobondW291H	Unknown results
2	Nitrile 68085	AD x 3 Coagulant gel	Nitrile 68073	Glove tested at InMat & Best *See Table 9*
3	Nitrile 68085	AD x 3 Coagulant gel		Glove tested at Best *See Table 9*
center	January 2004 Batch of Gloves			
1	Polyurethane	AD x 2	Nitrile PL 1172	Glove tested at Best *See Table 9*
2	Polyurethane	NP x 2	Nitrile PL 1152	Glove tested at Best *See Table 9*
3	Polyurethane	NP x 2	Nitrile PL 1152	Glove tested at Best *See Table 9*
4			Neoprene 671A	Glove tested at InMat *See Table 9 #307-36-02*
5	Polyurethane	AD x 2	Nitrile 68085	Glove tested at InMat *See Table 9 #307-20-11*
6	Polyurethane	NP x 2	Nitrile PL 1152	Glove tested at InMat *See Table 9 #307-37-03*
7	Polyurethane	NP x 2	Nitrile PL 1152	Glove tested at InMat *See Table 9 #307-37-04*

Notes:
   a) The designation of AD indicates Air D-Fense 2000R butyl based nanocomposite dried film. The designation of NP indicates Nanolok NP neoprene based nanocomposite dried film.

The gloves sent to InMat were tested both at InMat and Best Manufacturing. The results of these gloves are listed in Table 9 with some comparison testing.

Table 9. Solvent/Simulant[a] and OTR[b] Testing of Glove Prototypes

Glove	Description[c]	Gauge	OTR[d]	TEP[e]	CEPS[f]	TCE[g]	Acetone
		mil		Breakthrough (min) ASTM F39			
	Butyl rubber 874	16		>480	95	5.5	
	Chloroflex 723 Neoprene	28		ND	55	13.3	25.3
#2 11/03	Nitrile 68085/AD x 3/Nitrile 68073	9.5				5.3	
#1 1/04	Nitrile PL 1172/AD x 2 AD side tested	6.5		57.7	35.5		
#2 1/04	Nitrile PL 1152/ NP x 2 NP side tested	6			9.7	13.5	

#3 1/04	Nitrile PL 1152/ NP x 2 NP side tested	12			57.3	85.4	
#4 1/04	Neoprene 671A Only	12	792				
#5 1/04	Nitrile 68085/AD x 2	12	70				
#6 1/04	Nitrile PL 1152/ NP x 2	12	136				
#7 1/04	Nitrile PL 1152/ NP x 2 Duplicate	12	148				
#1 2/04	Nitrile PL 1152/ NP x 2	7		61	32	4	
#2 2/04	Nitrile PL 1152/ NP x 2/Neoprene	6.5		66		4	4

Notes:
  a) Solvent/Simulant testing performed by Best Manufacturing.
  b) OTR (oxygen transmission rate) testing performed by InMat.
  c) The designation of AD indicates Air D-Fense 2000R butyl based nanocomposite dried film. The designation of NP indicates Nanolok NP neoprene based nanocomposite dried film.
  d) OTR is oxygen transmission rate in cc/m^2 day atm @ 23C, 0% RH.
  e) TEP is the solvent triethylphosphate.
  f) CEPS is the mustard gas simulant 2-chloroethyl phenyl sulfide.
  g) TCE is the solvent trichloroethylene.

Because there was not enough testing on appropriate controls, it is hard to reach any quantitative conclusions from this data. Qualitatively, it was clear that a thin nitrile glove with one side coated with a thin nanocomposite barrier layer was not providing breakthrough time equivalent to the 16 mil butyl glove. Even though the process to make the gloves was well developed and significant qualitative information had been obtained, more complete testing was required. At this point, the modeling information was available which suggested that two layers of nanocomposite were critical in optimizing the breakthrough time. That modeling work and the testing of multilayer structures are described below.

Best Manufacturing began designing a proto-type dipping machine that will improve their dipping accuracy. After several meetings and discussions, it was determined that the timing for developing a prototype glove manufacturing line was much longer than expected. We also had difficulty in coming to an agreement with Best on how to proceed towards commercialization. Thus we did not have a second subcontract with Best in the second year. Instead, we focused on scale up of the Neoprene and Nitrile nanocomposite formulations, and have begun sampling alternative glove manufactures in addition to Best so that they can make prototypes and move forward towards commercial gloves.

7.4. Multilayer Modeling
Summary of Accomplishments

- Multilayer breakthrough time modeling has shown that by changing one or more of the interior layers to nitrile rubber, the thickness could be reduced to 6-10 mils while maintaining

the same breakthrough time. The outside of the glove could still be neoprene, and thus have its combination of flame, gasoline, and oil resistance.

- When barrier layers are combined with more permeable layers the breakthrough time depends critically on how the barrier layers are deployed
- The best way to deploy the barrier layers is to separate them as far apart as possible within the design limitations of the glove.
- The nanocomposite formulations developed by InMat provide a unique opportunity to utilize this effect on the breakthrough time, and a patent has been filed.

7.4.1.   Single Layers

The breakthrough time is approximately proportional to the thickness squared and inversely proportional to the diffusion constant for a uniform slab of a single material. [3] Thus thin films have a very short breakthrough time. When a very thin barrier coating is put on a very permeable substrate, the steady state permeation rate can be changed significantly, while the changes in breakthrough time can be much smaller.

The steady state permeation rate does not depend on how a thin barrier material is deployed on a more permeable substrate. This means that if the total thickness of the barrier material and substrate is the same, the steady state permeation rate will be the same for samples with a single barrier layer, or the barrier layer split into two or more coatings and separated by some or all of the more permeable substrate.

This is not the case for the breakthrough time. The breakthrough time can depend critically on the way the barrier material is deployed. In particular, if half the barrier layer is put on one side of the more permeable substrate, and the other half is put on the other side, there can be much larger increases in breakthrough time when compared with putting all the barrier material on one side.

The use of a clay nanocomposite approach to reduce the steady state permeation rate in polymers is well known. [4-5] The reduction is caused by the tortuous path a diffusing molecule must take in order to get around all of the clay platelets. This leads to a decrease in the effective diffusion constant parallel to the direction normal to the plates. In an idealized system whereby the permeant does not swell or significantly change the polymer, and whereby the permeant has no specific interaction with or absorption on the clay surfaces, the effect is geometric, and depends only on the aspect ratio, concentration, and detailed dispersion of the plates. It does not depend on what molecule is diffusing through the polymer, or the solubility and/or diffusion rate in the polymer. Thus the change in diffusion constant for a given polymer when a particular nanocomposite is formed can be estimated from measurements with a convenient permeant. The result can be used to estimate the change for permeants that might be more expensive to test.

The solubility of molecules in inorganic filled polymers is typically reduced by the volume fraction taken up by the inorganic. This is true when there is no specific absorption at the polymer – inorganic interface. In addition, the presence of the filler may reduce any polymer swelling that would otherwise occur when the diffusing molecule dissolves in the polymer. This could further reduce the solubility.

Specific absorption at the clay polymer interface may also modify the effectiveness of the clay platelet in blocking the diffusion of a molecule. This is because the absorbed layer may facilitate transport along (and therefore around) the surface of the clay platelet.

The diffusion constant and solubility of a polymer not only determine the steady state diffusion rate, but also determine the time it takes for a critical amount of material to get through the polymer (breakthrough time). Thus, an understanding of the effect of making a clay polymer nanocomposite on the diffusion constant should enable us to understand both the steady state permeation rate and the changes in breakthrough time. The relationship of those quantities for different permeants is extremely important to the area of chemical warfare agent protection. Typically permeants that are not hazardous are used to develop new materials and glove design, while the final testing is done with the actual agents. We will discuss how measurements of changes in gas permeation rates are related to changes in chemical warfare agent breakthrough times in the limit that we can ignore swelling of the polymer phase, and we can ignore specific absorption at the clay-polymer interface. The value of this work is that it will provide guidance as to how important both swelling and specific absorption are to the measured breakthrough times, and thus help us design improved materials. In addition, we will be able to show how the nanocomposite barrier layer is deployed within a multilayer glove can lead to large changes in observed breakthrough times.

In the steady state the permeation rate (flux) for a sheet of material of thickness t and permeability P that is maintained with a partial pressure difference for a single permeant of Δp is given by:

$$Flux = \frac{A * \Delta p * P}{t}$$

The permeability of a material is the product of the diffusion constant D, and the solubility S.

$$P = D * S$$

In a nanocomposite, both the diffusion constant and solubility can be modified. When exfoliated clay platelets are used as the filler, and when there is no specific absorption of the permeant on the clay, the presence of the clay will reduce the solubility by the volume fraction of clay present. Thus in a composite with volume fraction ϕ, the solubility S is given by the following equation where S is the solubility of the unfilled polymer.

$$S = (1 - \phi) * S_o$$

The Diffusion constant in a clay polymer nanocomposite can be approximated by the Cussler model [6] with the following equation:

$$D = D_o * \left(1 + \frac{(\alpha * \phi)^2}{(1 - \phi)}\right)$$

where α is the aspect ratio of the clay filler (i.e. the ratio of the plate thickness to its length or width), and where D_0 is the diffusion constant of the unfilled polymer. This result ignores many important features, but has been confirmed experimentally in several systems in that the roughly quadratic dependence on volume fraction is usually seen.
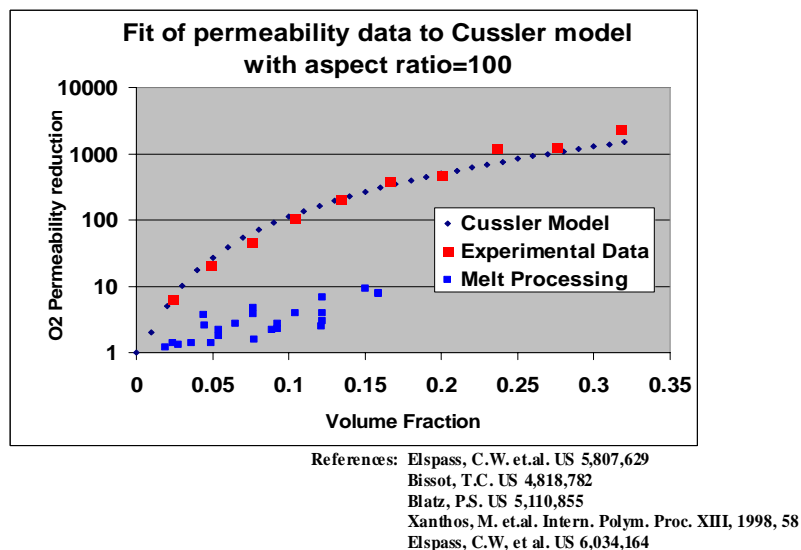
Another commonly used model is one originally developed by Nielsen [7] which predicts the following functional form for the change in permeability with filler concentration and aspect ratio:

$$D = \frac{D_o}{1 + \Phi * \alpha}$$

This model predicts much smaller reductions in diffusion constant than the Cussler model, and does not agree with the data developed by the InMat group on nanocomposite coatings.

The aspect ratio used in the above equations is often difficult to predict, as it is typically not the aspect ratio of individual clay platelets, but some effective aspect ratio that also depends upon the degree of dispersion in the final nanocomposite. The aspect ratio of individual platelets in the formulations used to make coatings that led to the data in the Figure 1 below was about reported at 10,000. The nanocomposite fits a curve which implies that the effective aspect ratio is closer to 100. [2]

Figure 1. Fit of Permeability Data to Cussler Model

References: Elspass, C.W. et.al. US 5,807,629
Bissot, T.C. US 4,818,782
Blatz, P.S. US 5,110,855
Xanthos, M. et.al. Intern. Polym. Proc. XIII, 1998, 58
Elspass, C.W, et al. US 6,034,164

7.4.2. Multilayer films

When a barrier film consists of more than one layer, the effective permeability of the total multilayer composite can be calculated from the permeability of the individual layers from the following equation:

$$\frac{t}{P} = \frac{t_1}{P_1} + \frac{t_2}{P_2} + \frac{t_3}{P_3} + \ldots$$

where P_1 is the permeability of the first layer, P_2 is the permeability of the second layer, etc., and t_1 is the thickness of the first layer, t_2 is the thickness of the second layer, etc.

When using barrier coatings to reduce the flux through a substrate, it is also useful to define the reduction in steady state flux as

$$R_{ss} = \frac{\left(\dfrac{t_1}{P_1}\right)}{\left(\dfrac{t}{P}\right)}$$

where layer 1 is defined in this case as the substrate layer on to which the barrier coatings are applied. It is important to note that when several barrier layers are used, the order does not change the steady state flux. The steady state flux doesn't change if a single barrier layer is broken into several thinner layers, as long as the total thickness of each material does not change.

### 7.4.3.   Transient behavior in single layer films

A complete description of the time-dependent permeation across a uniform film is given by the solution of the one-dimensional diffusion equation with appropriate initial and boundary conditions [3]. When swelling and concentration dependence of the diffusion coefficient can be ignored (normal or Fickian diffusion), the steady state solution is a uniform concentration gradient across the sample with a constant flow as given by the permeability relation described above. The transient behavior prior to achieving steady state can be described by a time-lag. The characteristic time dependence is shown in Figure 2. There is an initial period before the leading edge of the concentration of penetrating molecules has reached the second surface where the flow is insignificant followed by a smooth rise to steady state.
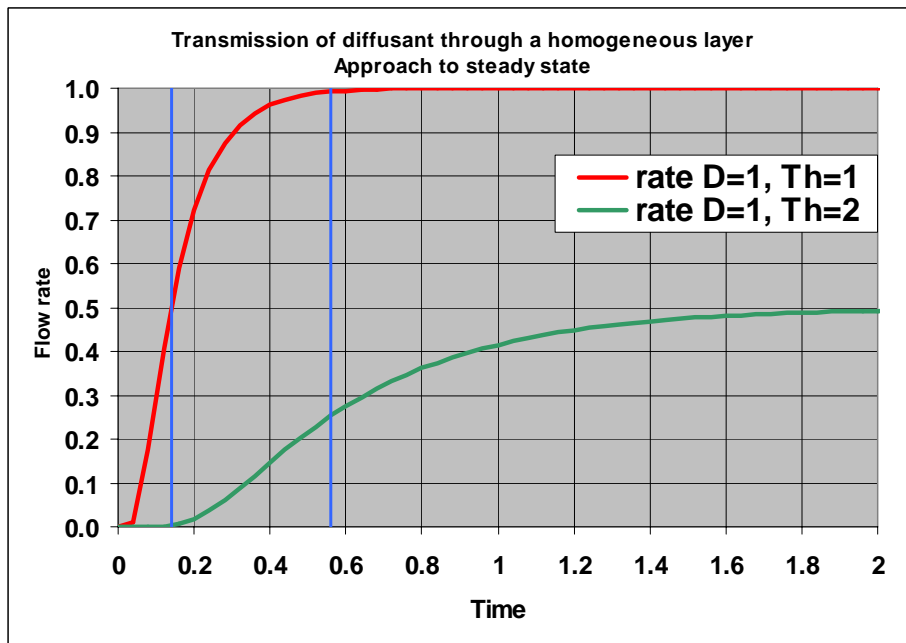
Figure 2

Figure 3 shows the time-integrated molecular flow. The linear (steady state) portion of the curve has an intercept on the time axis commonly referred to as the time lag T_{lag}, and given by

$$T_{lag} \quad = \quad \frac{t^2}{6D} \quad \approx \quad 0.1667 \, \frac{t^2}{D}$$

Diffusion through a homogeneous layer
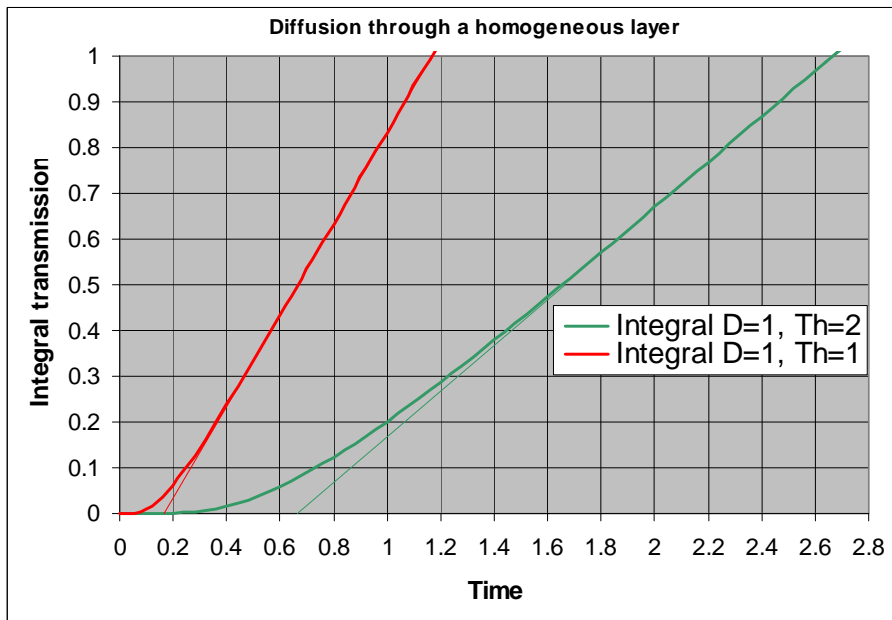
Figure 3

A different measure of the characteristic time scale of the approach to steady state is the time required to reach one half the steady state value.

$$T_{\frac{1}{2}} \quad \approx \quad 0.1388 \, \frac{t^2}{D}$$

For many chemical protection applications, what is important is a 'breakthrough time' which is defined as the time required to reach a predefined concentration (often the minimum detectable concentration) on the protected side of a barrier layer. Clearly the time-lag in the diffusion kinetics increases the breakthrough time beyond what it would be if the initial flow rate were equal to the steady state rate. Furthermore, as shown in Figure 2, a doubling of the layer thickness cuts the steady state flow by a factor of two but increases the time lag by a factor of four. Therefore the breakthrough time should be increased by more than a factor of two.

The time lag is dependent on the diffusion constant, not the solubility. Thus two films with equal permeability, one with twice the diffusion constant and the other with twice the solubility will have different time lags.

Another consequence of the time lag dependence on the diffusion constant only and not the solubility, is that careful transient flow measurements can provide determinations of both D and S.

### 7.4.4. Transient behavior in multilayer structures:

A complete description of the approach to equilibrium in such systems rapidly becomes mathematically quite intractable. Nonetheless, methods have been developed which allow the calculation of the time lag without having to solve the complete transient diffusion problem. [8-11] The time lag for a two layer laminate is given by

$$
T_{lag\,12} = \frac{\dfrac{t_1^2}{D_1}\left(\dfrac{t_1}{6\,D_1\,S_1} + \dfrac{t_2}{2\,D_2\,S_2}\right) + \dfrac{t_2^2}{D_2}\left(\dfrac{t_1}{2\,D_1\,S_1} + \dfrac{t_2}{6\,D_2\,S_2}\right)}{\dfrac{t_1}{D_1\,S_1} + \dfrac{t_2}{D_2\,S_2}}
$$

Note that the time lag expression for a laminate is dependent on the layer solubilities. The general expression for a three layer laminate may be expressed as shown under Figure 4 below.

The result is somewhat complicated, but some general observations are useful. First, the overall time lag is not affected by interchange of the outer layers which is another way of saying that the time lag does not depend on the direction of flow through the laminate. Second, the overall time lag is affected by interchange of the center layer with either of the two outer layers, i.e., the order of the layers. Remember that such an interchange does not affect the steady state permeability.

Figure 4

Three Layer Construction

Two Layer Construction
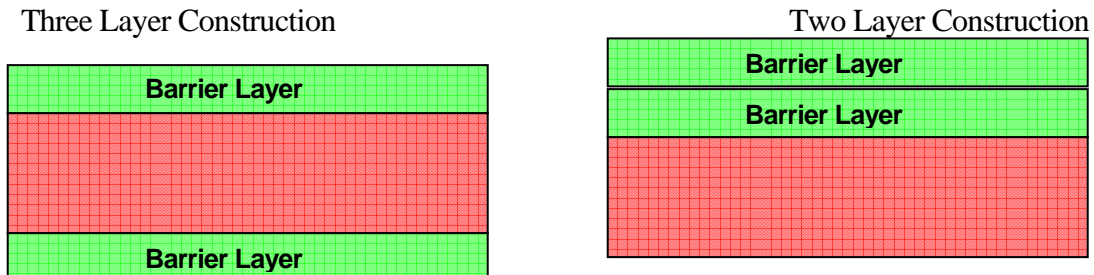
$$T_{lag\,123} = \frac{\dfrac{t_1^2}{D_1}\left(\dfrac{t_1}{6D_1S_1} + \dfrac{t_2}{2D_2S_2} + \dfrac{t_3}{2D_3S_3}\right) + \dfrac{t_2^2}{D_2}\left(\dfrac{t_1}{2D_1S_1} + \dfrac{t_2}{6D_2S_2} + \dfrac{t_3}{2D_3S_3}\right) + \dfrac{t_3^2}{D_3}\left(\dfrac{t_1}{2D_1S_1} + \dfrac{t_2}{2D_2S_2} + \dfrac{t_3}{6D_3S_3}\right) + \dfrac{S_2 t_1 t_2 t_3}{D_1 D_3 S_1 S_3}}{\dfrac{t_1}{D_1S_1} + \dfrac{t_2}{D_2S_2} + \dfrac{t_3}{D_3S_3}}$$

The example shown in Figure 5 is one where the outside layers provide the same steady state barrier properties as the inside layer, but where the diffusion constant (and thus steady state permeability) of the layers differ by a factor of 100.

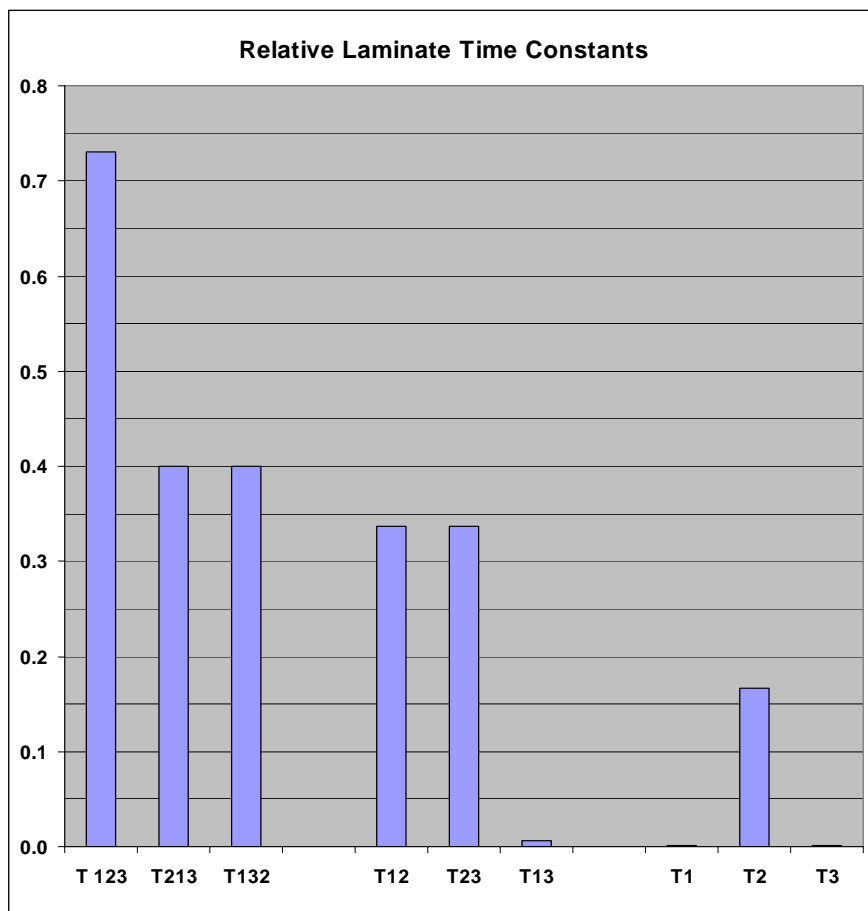| 3 layer formula from Barrie et. al. (1962)				T 123	0.73
				T213	0.4
				T132	0.4
Layer#	L	D	S		
1	0.01	0.01	0.1	T12	0.337
2	1	1	0.1	T23	0.337
3	0.01	0.01	0.1	T13	0.007
				T1	0.002
				T2	0.167
				T3	0.002

Figure 5

The thin outside layers, if used by themselves would have a very small lag time. On the other hand, when put on the thicker substrate, they lead to a significant increase in lag time. If they are put on one side, they increase the lag time by more than a factor of 2, and if put on opposite sides, the lag time is increased almost fivefold.

Figure 6 makes a similar point, as it shows the time lag for a three layer and two layer film having the same total amount of barrier coating. In this case, we plot the time lags as a function of the substrate (or central layer in the case of the three layer construction) thickness.

Figure 6 - Time Lag for Multilayer Films
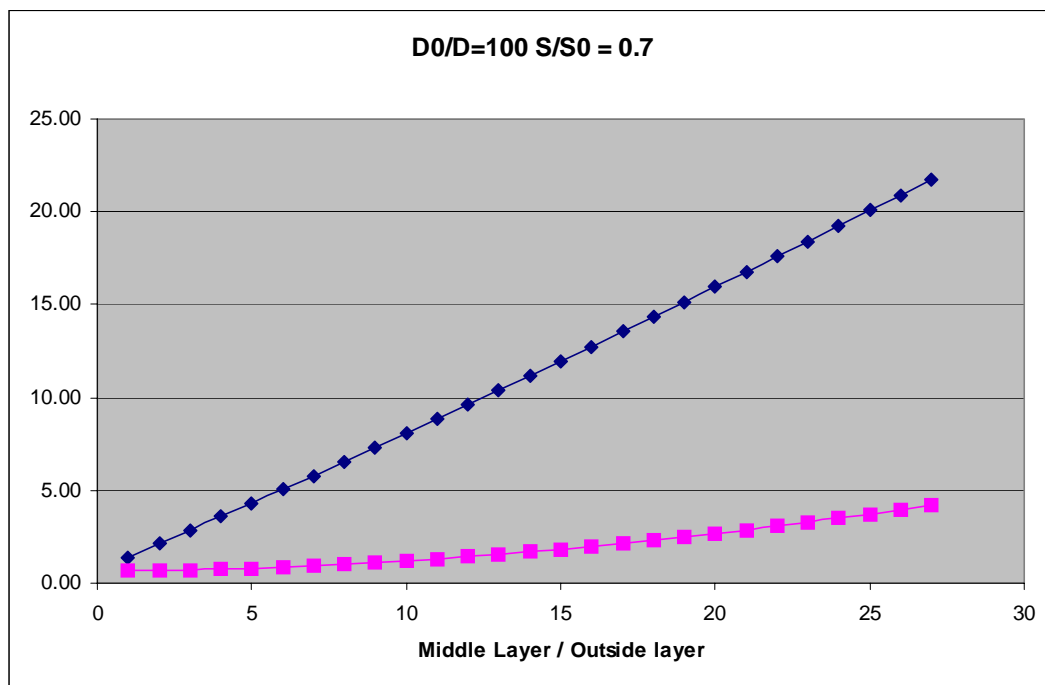
The conclusion from Figure 6 is that when the barrier layers dominate the permeability, the time lag will be almost linear in the thickness of the central layer in a three layer construction.

One way to estimate what the flux versus time curve will look like for a multilayer construction is to start with the data for a single layer, and rescale it using the calculated changes in lag time and steady state flux. We focus on the mustard gas results as all of these materials are relatively good barriers for nerve gas. Figure 7 shows the flux versus time for mustard gas as measured by Lindsay et al [12] for several gloves.

Figure 7

Mustard Gas Penetration Through Sample Gloves

Innovative Nanocomposite Materials
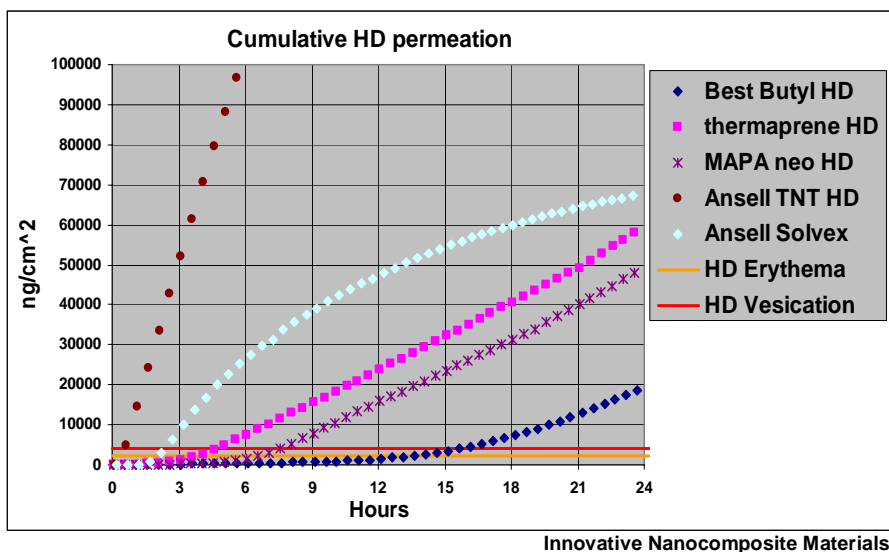
Using that data, we extracted a lag time and steady state permeation rate. Then using the equations in section 4.2, we determined the solubility and diffusion constant for mustard gas in each of the glove materials. The results are shown in the Table 10.

Table 10. Mustard Gas Permeation Property Comparisons

Glove	Thickness[a]	Lag Time[b]	Slope[c]	D/D_{butyl}	S/S_{butyl}	P/P_{butyl}
Butyl rubber	30	15	2200			
Neoprene (MAPA)	30	6	3000	2.5	0.5	1.4
Nitrile	4	0.25	7000	0.9	0.5	0.5

Notes:

 a. Thickness is in mils.
 b. Lag time is in hours.
 c. Slope in the Permeation rate in ngrams/m^2-hour).

Starting with the calculated diffusion constant and solubility for the 30 mil MAPA neoprene glove [12] we show the calculated flux versus time in Figure 8 for three coatings on that glove:
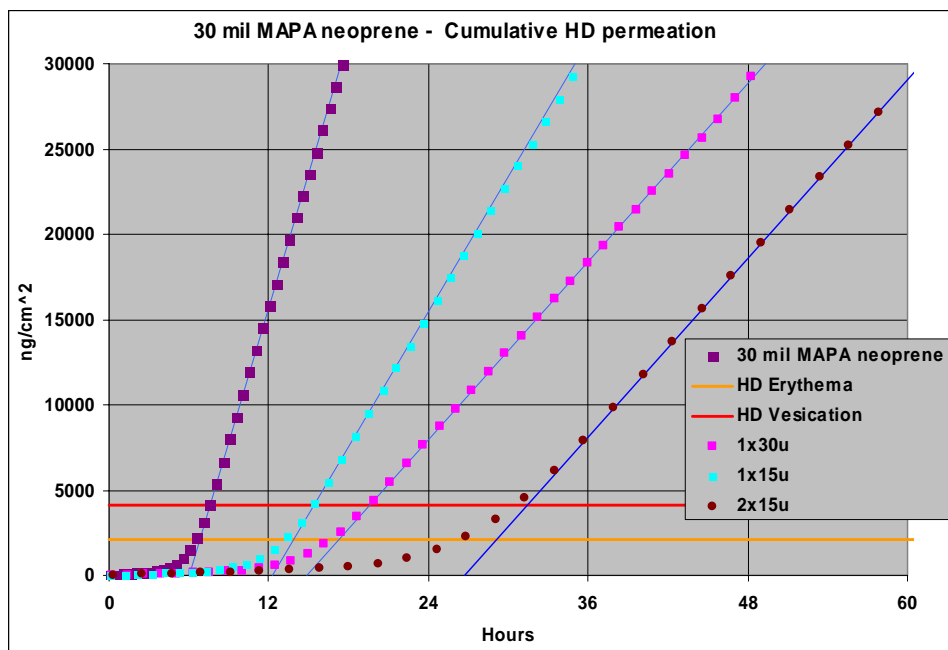
15 microns on one side

30 microns on one side

15 microns on both sides (total 30 microns)

23

The barrier layers were assumed to have 50 times lower diffusion constant than the MAPA neoprene, but the same solubility.

30 mil MAPA neoprene - Cumulative HD permeation

Legend:
- 30 mil MAPA neoprene
- HD Erythema
- HD Vesication
- 1x30u
- 1x15u
- 2x15u

X-axis: Hours (0, 12, 24, 36, 48, 60)
Y-axis: ng/cm^2 (0, 5000, 10000, 15000, 20000, 25000, 30000)

Figure 8

The calculations indicate that the three layer construction will have more than a 24 hour breakthrough time. It also shows how the lag time tends to dominate the breakthrough time in these materials.
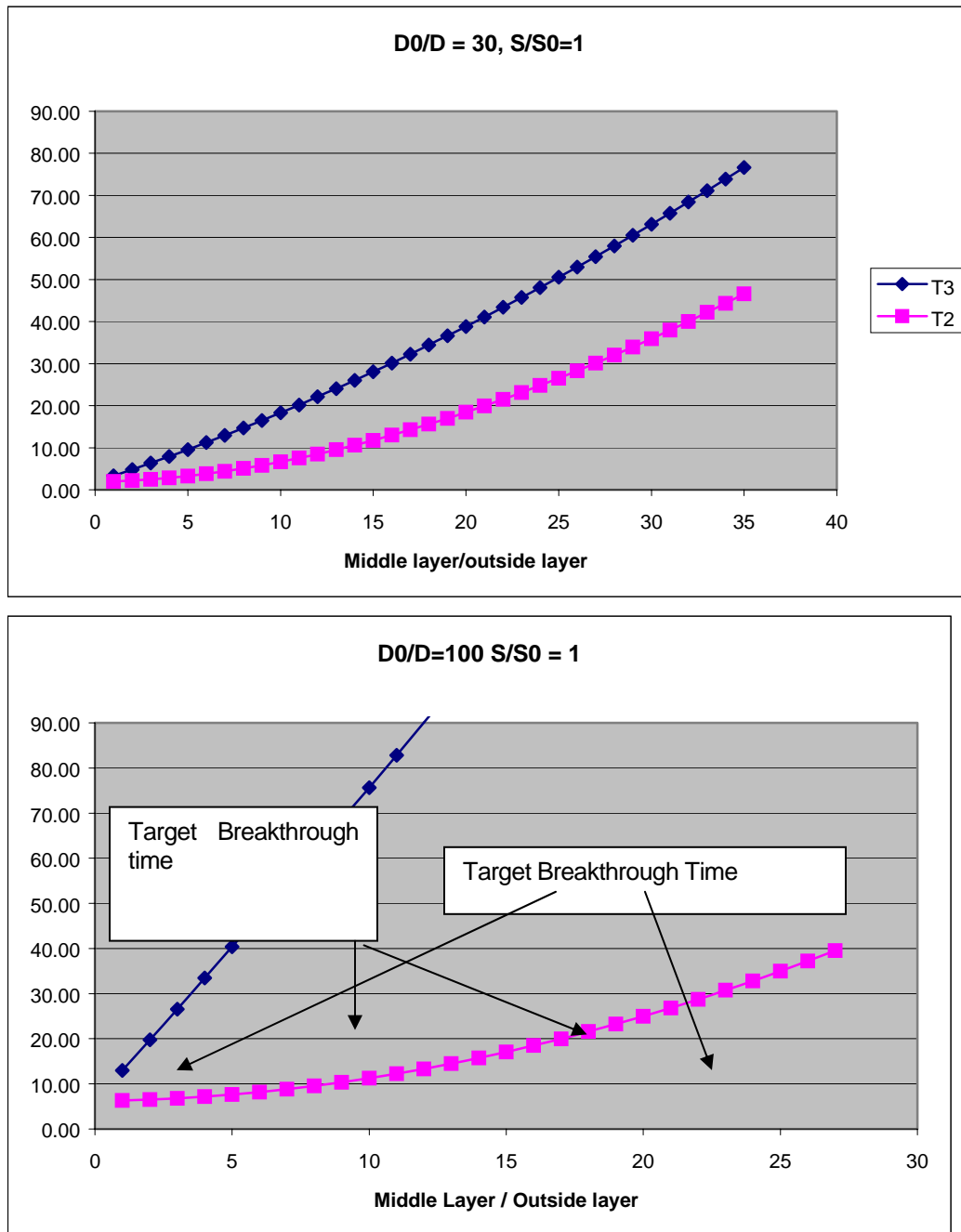
Since we have an estimate of the lag time for a thin nitrile rubber glove, [12] we have decided to use that in a model whereby the central layer is thin nitrile rubber, and the outside layers are 1 mil thick barrier coating with either 30 times lower diffusion constant or 100 times lower diffusion constant. The time lag for both a three layer structure and for a two layer structure with two mils of barrier coating on one side of the nitrile rubber are shown in Figure 9.

Since our target is 24 hours for the breakthrough time, we will assume that a thickness with a lag time of 24 hours would be a good starting point.

The curves in Figure 9 show that a three layer construction with a barrier coating only 30 times less permeable than the unfilled nitrile rubber could reach a 24 breakthrough time for mustard gas with a total thickness of about 15 mils (13 mils unfilled nitrile, 2 mils barrier material). A two layer construction would have to be more than 25 mils thick.

If we can reduce the permeability to mustard gas by a factor of 100 (as we have for oxygen), then a three layer construction is even more advantageous. In that case, the model indicates that about 5 mils (3 mils central layer, 2 mils barrier coating) is all that might be needed. On the other hand, a two layer construction would have to be more than 20 mils thick. This is shown in the second part of Figure 9.

Figure 9

D0/D = 30, S/S0=1

Legend: T3, T2

X-axis: Middle layer/outside layer

D0/D=100 S/S0 = 1

Target Breakthrough time

Target Breakthrough Time

X-axis: Middle Layer / Outside layer

7.5. Multilayer testing

Summary of Accomplishments

- A Sample containing five layers based on neoprene and neoprene nanocomposites with a total thickness of only 13 mils have been shown to provide the same breakthrough time for CEPS (2-chloroethyl phenyl sulfide, mustard gas simulant) as a 16 mil butyl glove.

- Two thin nanocomposite layers separated by 12 mils of neoprene provide large (> 10 times) increases in breakthrough time for mustard gas simulant CEPS based on testing of a five layer design.
- Five layer samples with a total thickness of 13 and 20 mils containing only neoprene and neoprene based nanocomposite have been made and tested. The thinner sample had a CEPS breakthrough time essentially equal to that of a 16 mil butyl glove. The thicker sample had a breakthrough time almost twice as long.
- The data in combination with multilayer modeling indicate that a glove containing only neoprene polymer and neoprene nanocomposite layers that has similar breakthrough times to a 16 mil butyl glove, but that is only 12.5 mils thick is feasible. Changing one or more of the inner layers to nitrile rubber (outside layers as neoprene) could enable the total thickness to be reduced to 6-10 mils.

       7.5.1.   Helium testing of multilayer structures

Natural Rubber / Butyl nanocomposite multilayers

The principals outlined in the modeling have been demonstrated with helium permeability measurements using an internally developed apparatus. Prior to a measurement, a sample is thoroughly degassed from both sides with a vacuum pump. The system determines gas transmission through a sample by exposing one side of the sample to a step change in gas pressure and measuring the rise in pressure in a known volume on the other side of the sample with a capacitance manometer. The pressure vs. time data is acquired and a numerical derivative calculated which is used to determine both the steady-state permeability and the initial kinetics of the gas transmission.

The samples measured in this study were prepared using thin gauge (nominal 0.030") natural latex rubber sheet. Three samples were spray coated with AD2000 and allowed to air dry. Two of these were then given a second spray coating, one on the same previously coated side and the second on the reverse side. An attempt was made to have each coat deposit the same amount of material. The data for these samples are summarized in Table 11 and Figures 10 and 11.

Table 11. Experimental & Calculated Helium Transmission Rates

Sample	Experimental		Calculated	
	T ½*	Helium transmission rate*	T ½*	Helium transmission rate*
natural rubber control	1	1	1	1
Coated A	2.4	0.29	2.4**	0.29**
Coated AA	2.7	0.20	2.7	0.17
Coated AB	6.2	0.21	8.9	0.17

*All data shown are relative to the values for uncoated natural rubber 0.8 mm thick.
**The relative diffusion constants and solubility needed for the model calculations were obtained by fitting the coated A sample data. Thus these calculated values are constrained to fit the experimental values.

Figure 10.

He transmission - AD2000 coated natural rubber

Figure 11.

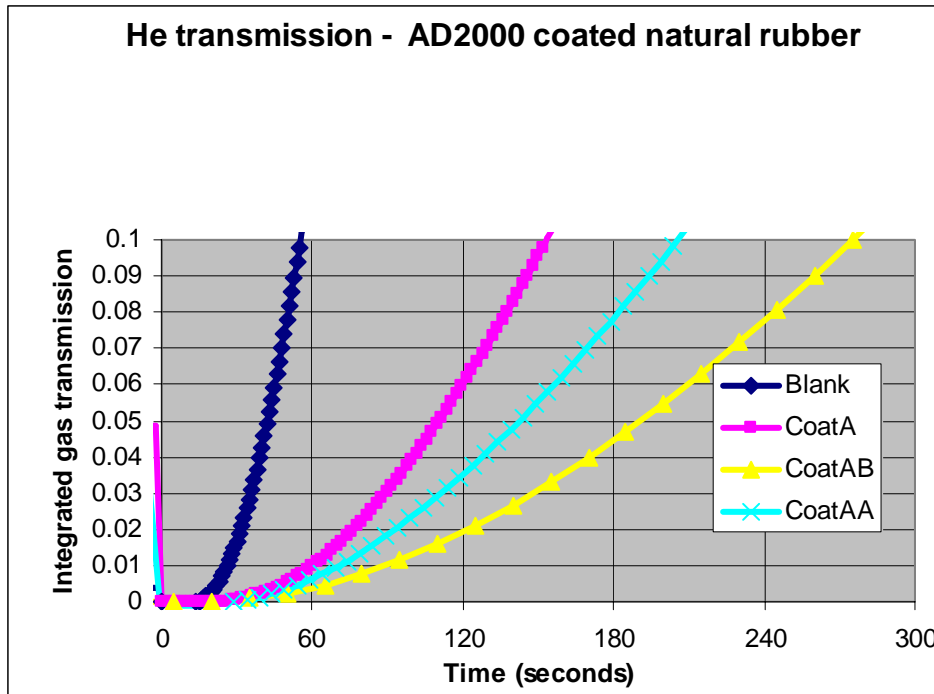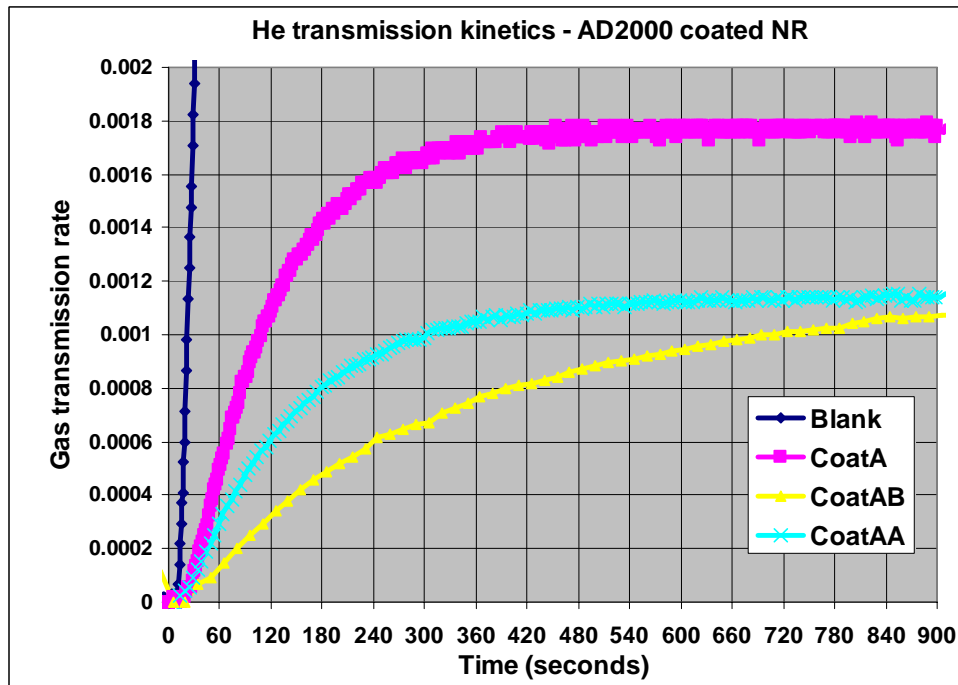He transmission kinetics - AD2000 coated NR

The data shows that putting a coating on two sides of the sample instead of on one side increases the time it takes to reach half the steady state permeation rate by more than a factor of 2. The lag times obtained by extrapolating the long time integrated gas flux back to the intercept with the time axis are also increased by more than a factor of 2.

In order to determine a breakthrough time, one needs to pick a threshold value of the integrated gas flux. Using the data shown in Figure 10, any choice of integrated flux between 0.01 and 0.09 has the breakthrough time increasing by between 32% and 45%. This is a significant increase, although much lower than expected from both the modeling and the measured half time to steady state and the lag time. The reason for this is a combination of measurement sensitivity at low integrated flux, coating inhomogeneity, and possible defects in the coating. Nonetheless, the data demonstrates the effectiveness of using two nanocomposite coatings separated by a permeable layer in providing significant increases in breakthrough time.

Neoprene / Neoprene nanocomposite multilayer structures

We also made laboratory samples of multilayer neoprene / neoprene nanocomposite as an example of what we hope the glove companies will use in a protective glove design. This work was done by spray coating flat sheets. Thickness control was difficult, and is the largest source of error when comparing with the modeling results.

We compared two thicknesses of unfilled neoprene with two multilayer neoprene structures. The structures used are shown in Figure 12

Figure 12. Multilayer Neoprene Structures
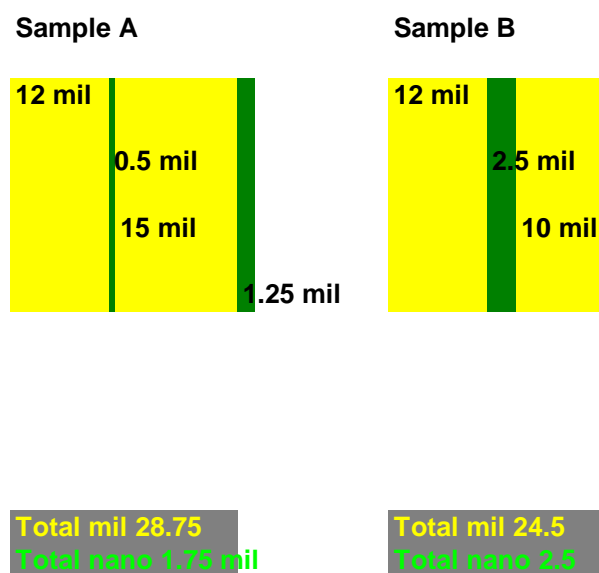
The thicknesses shown in Figure 12 were the target thicknesses. The actual thickness of sample A came out to 30 microns (very close to the target) but sample B was only 19.5 microns thick.

The same multilayer modeling discussed in the previous section (but generalized to cover up to five different layers) was used. The control neoprene results were used to fix the solubility and diffusion constant of neoprene. The steady state helium permeation was used to determine the change in the diffusion constant in the nanocomposite layers. It was found to be about 100 times lower than the

unfilled neoprene. The target thicknesses of sample B were reduced by a constant factor so that the total thickness matched the measured thickness. The lag times and steady state permeability of each sample was then calculated and compared with the measured half time for reaching steady state. These are not the same as in a homogeneous sample. They are simply proportional to each other. If we assume that is approximately true here also, than the procedure described above can be used to assess the utility of the modeling. These results are summarized in Table 12.

Table 12. Helium Transmission Rates of Neoprene & Neoprene Nanocomposites

Sample	$T_{1/2\,exp}$	T_{lag}	Helium transmission rate*		Total Thickness
	seconds	seconds	Experiment	Calculated	mil
Control 1	17	17	0.49	0.49	16
Control 2	43	45	0.28	0.30	26
B	120	64	0.030	0.025	19
A	250	282	0.045	0.041	30

* Helium transmission rate in relative values in arbitrary units.

The primary conclusion that can be drawn from this experiment is that even though sample B has much more barrier coating, and lower steady state permeability than Sample A, it will have a much shorter breakthrough time.

7.5.2. Stimulant and Solvent Testing of multilayer samples

Although we agreed upon an experimental design with Best Manufacturing that should have enabled us to reach firm conclusions as to the relative effectiveness of our three candidate barrier coatings, the results were inconsistent and will only enable qualitative conclusions to be reached. At this time we cannot be sure if the problem is variability in layer thickness or errors in the breakthrough time measurements. Nonetheless, let us discuss the conclusions we can reach based on the data we have obtained from Best Manufacturing shown in Tables 13, 14 and 15. These conclusions are also based on the insights we have obtained from our multilayer modeling.

Table 13. Modeling/Simulant Test Matrix - InMat Nanocomposites in Multilayer Cast Films

Test #	1	2	3	4	5	6
Material	**mils**	**mils**	**mils**	**mils**	**mils**	**mils**
Neoprene	4	4	4	4	4	4
Nanolok NP	0.5	0.5				
Air D-Fense 2000R			0.5	0.5		
Nanolok NT					0.5	0.5
Neoprene	6	12	6	12	6	12
Nanolok NP	0.5	0.5				
Air D-Fense 2000R			0.5	0.5		
Nanolok NT					0.5	0.5
Neoprene	4	4	4	4	4	4
Target Total mils	15	21	15	21	15	21

Breakthrough time (min)						
Triethylphosphate (TEP)	>480	>480	>480	>480	>480	>480
Trichloroethylene (TCE)	9	9	9	13	13	17
2-Chloroethyl phenyl sulfide (CEPS)	93	173	125	405 203	101 57	153
Acetone	21.4	41	53	141 87	9.3 21	21
Actual Total mils	13	20	14	24	13	21
Oxygen Transmission Rate (cc/m^2 day atm @ 23C, 0% RH)	32	28	44	44	25	15
Calculated Barrier Coating (microns)	52	58	61	59	47	78

Table 14. Modeling/Simulant Test Matrix – Control Cast Films

Test #	7	8	9	10
Material	mils	mils	mils	Mils
Neoprene	4	4		
Nitrile			4	4
Neoprene	6	12		
Nitrile			6	12
Neoprene	4	4		
Nitrile			4	4
Target Total mils	14	20	14	20
Breakthrough time (min)				
Triethylphosphate (TEP)		>480	>480	>480
Trichloroethylene (TCE)		4.2	12.9	13
2-Chloroethyl phenyl sulfide (CEPS)		14.2	30.3	133
Acetone		5.4	10.3	13
Actual Total mils		11	13	17
Oxygen Transmission Rate (cc/m^2 day atm @ 23C, 0% RH)		1304	224	183

Table 15. Modeling/Simulant Test Matrix – Control Gloves

Test #	Butyl Rubber 874	Chloroflex 723 Neoprene
Material	mils	mils
Breakthrough time (min)		
Triethylphosphate (TEP)	>480	
Trichloroethylene (TCE)	5.5	13.3
2-Chloroethyl phenyl sulfide (CEPS)	95	55
Actual Total mils	16	28

The thickness of each layer was not measured, but was a target thickness based on the casting technique. Measurements of the thickness of the final multilayer structure show that the thickness has

a large amount of variability. This may account for some of the results, and the fact that repeat measurements of nominally the same sample led to breakthrough times that changed by about a factor of 2. In addition, the two nitrile rubber controls should differ in breakthrough time by about a factor of 1.7-2 (if lag time dominates) and a factor of 1.3-1.4 (if permeation rate dominates). All the breakthrough time measurements on the two thicknesses of nitrile rubber should have a ratio of between 1.3 and 2, but all three are outside it. Despite our concerns as to the accuracy of the measurements, we will do our best to draw some conclusions.

For the purposes of this discussion, we will focus on the CEPS data. The CEPS data was chosen because all samples performed well against TEP and the TCE and acetone results are more important to commercial applications.

The most important conclusion is that all the nanocomposite containing samples (except test 5 in Table 13) provided similar or larger breakthrough time for CEPS when compared to a 16 mil butyl glove. Even an entirely neoprene sample with only 6 mils of neoprene in the central layer had a comparable breakthrough time. This demonstrated that a multilayer design with two nanocomposite layers separated by a central layer will be able to provide the targeted performance.

7.5.3. Suggested designs for minimizing thickness and maximizing breakthrough time:

Using a spreadsheet that models five layer structures, we find that if we make the outside layers only 1 mil thick instead of 4 mils thick, we would have reduced the breakthrough time of test 1 from Table 13 (with a 6 mil central layer) by about 35%. This loss can be completely recovered by adding 2.5 mils of neoprene to the central layer. Thus we estimate that a glove with 1 mil of neoprene on the outside, 1 mil of neoprene based nanocomposite on the other side, and a central layer of 8.5 mils (total thickness of 12.5 mils) would have similar simulant breakthrough times as a 16 mil butyl glove. This is a significant reduction from the 15 mil design that was tested, although very similar to the total thickness of 13 mils that was measured.

If we look at the three control measurements, one would conclude that the nitrile rubber used is 5-10 times less permeable than the neoprene to CEPS. Using this in our model, we can estimate the effect of replacing the central layer with nitrile rubber. Our models indicate that this would allow for the central layer to be 2.5 mils thinner, and thus a glove of about 10 mils in total thickness. If nitrile or butyl based nanocomposite (which should be more effective against CEPS than the neoprene nanocomposite) is also used, then it may be possible to reduce the central layer thickness by up to an additional 4 mils, leading to gloves that are only 6 mils thick.

These estimates should only be viewed as rough calculations for what might be possible. The data we have right now is not complete enough to allow for detailed modeling. All that has been done is to use the information we have to make reasonable guesses as to what the relative diffusion constants might be in the different materials, and then explore the implications for multilayer glove designs. Additional samples and testing will be required before a glove design can be finalized.

7.6. Key Issues for full commercialization
We have not made glove prototypes with the optimal designed barrier coating layer using a neoprene base. The major issue is the glove dipping process development, and the associated thickness uniformity and control. Another issue is the overall adhesion between the different layers. Laboratory

work done at InMat indicates that this last issue has been somewhat resolved using improved nitrile formulations, but the final test will require a glove manufacturer to make prototype gloves for testing.

Another issue that has arisen during our recent wider sampling of the protective glove industry with these formulations is the shipping stability of the neoprene formulations. Although early shipments to Best were stable, more recent shipments to other glove companies agglomerated during shipment. Neoprene is well known to be a marginally stable dispersion and our nanocomposite exhibits many of the same problems as the original raw material. We believe the shipping instability recently observed may be due in part to variations in the raw material and/or changes in it with time. Further work on this will be needed before the neoprene formulations can be fully commercialized.

The nitrile nanocomposite formulations are much more robust and stable. We can now produce product using raw materials from two different suppliers. These coatings can be used in conjunction with neoprene glove formulations and are currently the best option for producing a chemical protective glove that is intrinsically less flammable and sensitive to petroleum oils than the current butyl gloves.

Finally, it is worth commenting on other applications of these materials. The intrinsic oil and gasoline resistance make them good candidates for gasoline hoses. Improved barrier in this product is critical to reducing overall VOC (volatile organic content) emission from vehicles and gasoline engines.

These materials may also offer adhesion, cost, and performance benefits over the earlier butyl rubber technology for gas and air barriers. The raw material costs are lower, and the nitrile rubber matrix is much easier to cure than the butyl rubber matrix.

8. Summary: Technical Feasibility

In the first year of this contract, we demonstrated that neoprene and nitrile nanocomposite coating formulations could be developed that provided barrier properties comparable to butyl nanocomposites, while having superior petroleum oil resistance. In addition, it was expected that a neoprene based material would have superior flame resistance due to the halogen content and intrinsic properties of neoprene. Both neoprene and nitrile rubber stick well to the neoprene currently used in the protective glove industry, and thus these materials were chosen as the prime candidates for use in multilayer glove design.

The second major accomplishment in the first year was the modeling of multilayer barrier structures that contain thin nanocomposites. These structures are unique in that they have layers which have similar chemical compositions (e.g., only neoprene polymer) but which have effective diffusion constants that can differ by factors of 30-100. Our modeling work showed that these structures can have very large increases in breakthrough times when the thin barrier layers are separated by as large a distance as possible.

In our second year, we extended our modeling efforts, presented the results at a conference, and filed a patent on the use of nanocomposite multilayer structures to provide large increases in breakthrough times. In addition, we demonstrated the concept by fabricating multilayer structures using neoprene and neoprene nanocomposites, and measured the permeation rate and breakthrough time for helium.

In addition, a major part of our effort in the second year involved the process for making larger quantities of neoprene and nitrile nanocomposites. Two unexpected issues arose: the stability of neoprene latex leading to process issues in making nanocomposites, and the availability of the nitrile latex that had been used in the first year efforts. Both of these required a lot more formulation effort in order to produce these materials in a quantity and reproducibility suitable for customer sampling. Our glove partner, Best Manufacturing, did not move as quickly towards making prototypes as we had hoped (this was only in part due to our own supply problems) and other glove manufacturers were sought and identified. Work is underway at alternative glove companies.

The key accomplishments of this program are:

- Development of two new nanocomposite barrier coatings, one based on neoprene and the other based on nitrile rubber, that are being tested for use in chemical protective gloves.
- Filing of a U.S. patent and an international application (WO 2005/061608 A1) to add additional protection to this formulation technology (already covered by InMat's basic U.S. patents 6,087,016 and 6,232,389).
- Scale up of coating formulations to sample customers.
- Glove prototype testing of the new formulations by a leading glove manufacturer.
- Demonstration of improved breakthrough time using both of these new formulations.
- Multilayer modeling of transport and calculation of lag times demonstrating the importance of multilayer design to optimizing breakthrough time.
- U.S. patent filed on use of nanocomposite barrier coatings in optimized multilayer designs.
- Presentation of modeling and initial results to the CBD conference in Maryland, December 2004.
- Use of helium testing to verify models and identify key issues such as coating uniformity and adhesion in practical applications.
- Qualification of two raw material suppliers for the production of nitrile rubber nanocomposites.

Despite all this progress, additional work is needed on the glove manufacturing process. Optimized multilayer prototypes have not yet been produced and tested for breakthrough time with chemical warfare agents. It is expected that with a modest amount of cooperative work with a glove manufacturer, exciting new chemical protective gloves that meet the needs of the Defense department can be developed. Commercially useful chemical protective gloves and other commercial applications of the technology developed in this program will also be developed.

9. References

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